

**ADMINISTRATIVE RECORD**

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1070101ASARCO

0071072

MEMORANDUM



1264372 - R8 SDMS

**CHM HILL**

TO: Doug Lovell/DEN

FROM: Tom Sale/DEN

DATE: May 7, 1985

RE: ASARCO First Quarterly Groundwater Sampling Data,  
January 15 through 21, 1985; Impact of Turbidity  
on Metal Ion Concentrations

PROJECT: W68230.00

INTRODUCTION

Groundwater monitoring wells DH-1 through DH-11 at the ASARCO facility in East Helena, Montana, were sampled between January 15 through 21, 1985. Samples obtained from the wells contained large amounts of turbidity. Subsequent to the sampling, concerns regarding the turbidity and its effects upon the representativeness of total dissolved metal samples have been voiced by Systems Technology, Inc., Hydro-metrics, and the Montana State Department of Health and Environmental Sciences. These concerns center around the following issues:

1. Due to high turbidity, some metals samples were allowed to stand for 1 to 3 hours prior to preservation. During this time, exposure of the sample to an oxidizing environment and changes in sample pH may have significantly altered the chemical equilibrium of the samples and caused significant changes in concentrations of some dissolved metal ions.
2. Potentially the material imparting the turbidity to the samples has the ability to absorb metal cations from the aquifer water while desorbing cations which are less preferentially held. These surface reactions may have altered the dissolved metal ion concentrations of the samples.

The following discussion attempts to provide sufficient information to evaluate these issues. This includes: discussion of the physical processes involved with each issue, a review of pertinent literature, and conclusions

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regarding the representativeness of the January 1985 ground-water water quality data. The final portion of this memorandum summarizes the information presented and provides recommendations concerning future samplings.

#### SAMPLE PRESERVATION

The effort of collecting a representative water quality sample is futile if chemical reactions occur that alter the character of the water between the time the sample is collected and analyzed. Commonly, the chemical environment of groundwater is reducing (lacking oxygen) and saturated with  $\text{CO}_2$ . As a sample is removed from this environment to the surface, oxygen enters the sample, causing an increase in the oxidizing potential of the sample (Eh) and  $\text{CO}_2$  will tend to gas out of the sample causing an increase in pH ( $-\log[\text{H}^+]$ ).

Figure 1, copied from HEM (1970), presents a pH-Eh species predominance diagram for iron. The highlighted box in the center of the diagram shows the normal range of pH and Eh. The figure indicates that as pH and Eh increase insoluble ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ) becomes the dominant species. Most metal cations behave in a similar fashion with insoluble precipitates tending to form at high Ph and Eh values.

In order to inhibit the formation of insoluble metal precipitates during sample storage, the sample's pH is lowered to less than two. At this pH soluble metal cation species predominate (see Figure 1). If the parameter of interest is total dissolved metals, it is also necessary to filter water samples prior to acidification. If this is not done, large amounts of metal precipitates which exist in association with suspended solids will be dissolved and erroneous values of total dissolved metals will be obtained.

Water samples obtained from the ASARCO monitoring during the first samplings round contained high turbidity and required filtrations for determination of total dissolved metals. Some samples were allowed to settle from 1 to 3 hours to reduce the time and effort required for filtration. During this time the reaction previously discussed may have occurred and altered the metal ion concentrations in the samples.

Data presented in Hydrometric's letter of February 19, 1985, to John Nickel of ASARCO (Attachment A) shows the variations in sample pH with time for seven samples (Table 1). This



Figure 1

ph-Eh Species Predominance Diagram  
for Iron

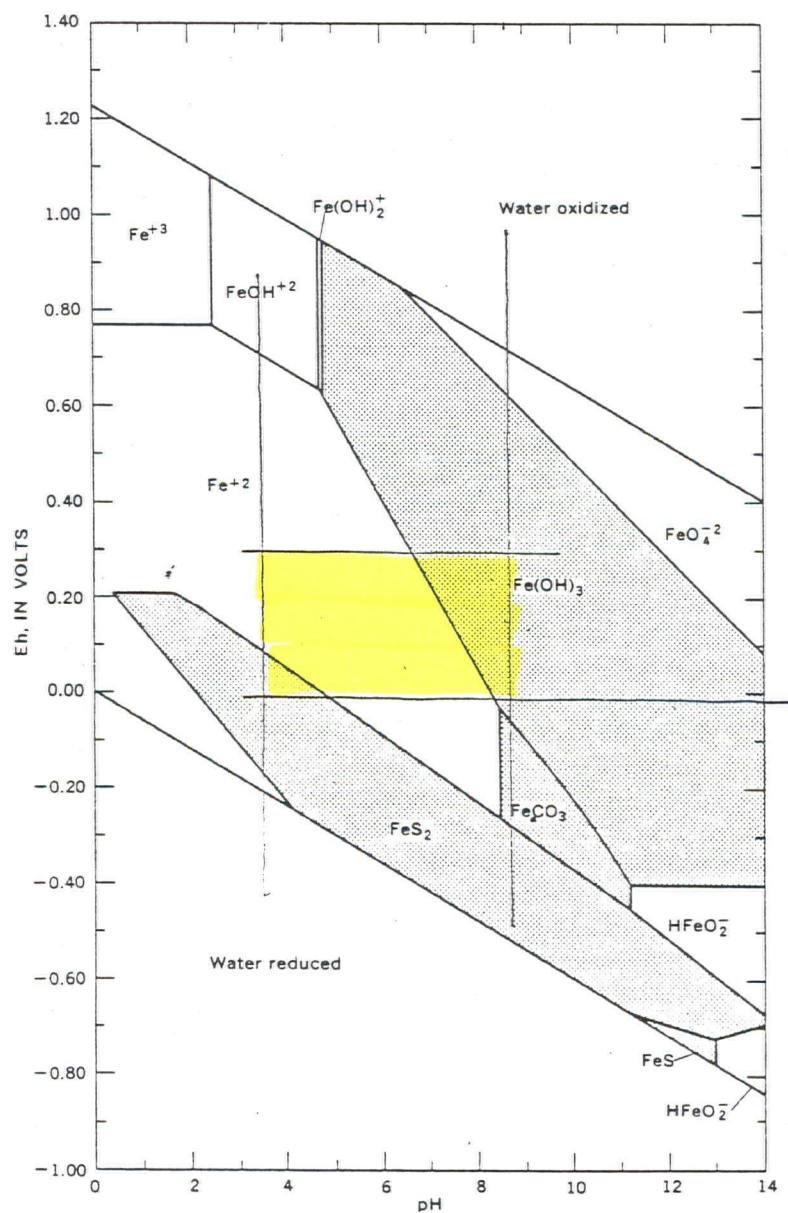


FIGURE 14.—Fields of stability for solid and dissolved forms of iron as function of Eh and pH at 25°C and 1 atmosphere of pressure. Activity of sulfur species 96 mg/l as  $\text{SO}_4^{-2}$ , carbon dioxide species 1,000 mg/l as  $\text{HCO}_3^-$ , and dissolved iron 0.0056 mg/l.

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data shows that out of seven samples, the pH of one decreased significantly after 45 minutes and two increased significantly after one day. One question raised by this data is whether the samples pH varied in the first 10 minutes. Personal experience has shown that pH values in some groundwater samples will increase rapidly in the first few minutes after sampling and then stabilize. Due to the lack of information on sample pH immediately after sampling, and the fact that some of the sample's pH varied with time, it is difficult to conclude what impact the delay in preservation had, with respect to chemical precipitation reactions controlled by pH.

Table 1  
PH MEASUREMENTS OVER TIME

Sample No.	Time Coll.	Date	pH 1st Read. (~10 min.)	$\Delta$ pH	pH 3rd Read. (1 day)	$\Delta$ pH
AEH-8501-118	9:30 a.m.	1/18/85	7.65	0	7.90	+.25
AEH-8501-124	11:30 a.m.	1/18/85	7.70	+.01	7.70	0.0
AEH-8501-117	12:30 p.m.	1/18/85	7.78	+.01	7.88	+.10
AEH-8501-122	3:00 p.m.	1/18/85	7.69	-.04	7.65	-.04
AEH-8501-125	4:30 p.m.	1/18/85	7.97	-.26	7.70	-.27
AEH-8501-121	9:30 a.m.	1/19/85	7.70	-.01	7.69	-.01
AEH-8501-126	4:20 p.m.	1/21/85	7.49	+.03	7.55	+.06

Note: In all cases, sample temperatures and buffer temperatures are the same.

Delays in sample preservation may also have allowed changes in sample Eh to cause precipitation reactions. This change in Eh would only be possible if a difference existed between the oxidation-reduction condition within the aquifer and the surface. Water quality data presented in the Systems Technology Inc. memorandum of April 30, 1985 (Attachment B), and copied in Table 2 suggest that the oxidation-reduction within the aquifer is similar to that of a surface water. This is indicated by the values of total iron (EPA) and dissolved iron (ASR). Large amounts of total iron are present in the sample, but only small amounts of dissolved iron (6.3 to 130 ug/e) exist in solution. These concentrations are typical of a surface water with a neutral pH. Since it



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appears that the sample Eh remained stable, it is likely that precipitation reactions associated with changes in Eh did not occur.

Table 2  
 COMPARISON OF USEPA & ASARCO METALS DATA

Well No.	As		Cd		Cu		Fe		Pb		Mn		Zn	
	EPA	ASR	EPA	ASR	EPA	ASR	EPA	ASR	EPA	ASR	EPA	ASR	EPA	ASR
DH-2	26	8.	<4.	<1.	61	z8.	18,300	25.	45	<5.	247	19.	349	110
DH-3	7.8	7.	<4.	<1.	6.4	<8.	111	6.3	4.6	<5.	101	120	156	180
DH-3R	5.4	7.	<4.	3.	18.	<8.	5,780	25.	11	<5.	196	100	155	170
DH-7	99	5.	<4.	<1.	343	<8.	62,500	25.	51	<5.	4,390	41	341	11
DH-9	22,000	6.	500	5.	5,500	13.	219,000	130	26,000	<5.	12,400	2,800	48,100	580
DH-10	5,800	5,100	<z4.	3.	156	9.	16,600	63	170	z<5.	4,310	4,800	551	71

Work done by the Illinois State Water Survey, 1981, investigated the effects of delayed sample preservation upon the concentrations of seven metal cations. The results are presented in Table 3. These show that Ca, K, Mg, Mn, and Na were not significantly affected by the delays in sample preservation. This is not surprising due to the fact that these species tend to form insoluble precipitates only at high pH's and concentrations. In contrast, concentrations of Fe and Zn showed dramatic decreases with delays in sample preservation. Additional metal ions which may behave similar to Fe and Zn include Al, Cr, and Cu.

Based upon available information, it is not possible to quantitatively evaluate the impact of the delays in sample preservation which occurred during the first quarterly sampling round of groundwater monitoring wells at ASARCO. The only statement that can be made is that it is possible that significant changes in water chemistry occurred during the delays in sample preservation and that these changes in water chemistry may have allowed for precipitation reactions to occur which reduced the concentrations of some dissolved metal ions (i.e., Fe, Zn, Al, Cu, and Cr).

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Table 3  
 SITE 5-BRD and 6-DUP: ANALYSIS OF THE TENTH WELL VOLUME  
 SAMPLE USED FOR STORAGE STUDY  
 (CONCENTRATIONS IN mg/L)

Site 5-BRD

Hours after collection- before preservation	pH	Ca	Fe	K	Mg	Mn	Na	Zn
0	6.7	111.	11.6	32	44.6	3.81	186	0.18
7	7.0	110.	0.33	31	41.9	3.15	172	0.02
24	7.0	104.	<0.03	35	41.4	3.10	181	0.02
48	7.0	99.	0.03	33	39.5	2.98	171	0.02

Site 6-DUP

Hours after collection- before preservation	pH	Ca	Fe	K	Mg	Mn	Na	Zn
0	6.8	32.5	5.74	189	94.2	ND*	215	ND*
7	7.2	35.2	<0.08	203	110.	ND*	242	ND*
24	7.2	32.0	<0.08	204	96.6	ND*	223	ND*
48	7.2	30.1	0.34	184	89.1	ND*	204	ND*

\*ND = not detectable.

ADSORPTION-DESORPTION BY COLLOIDAL MATERIALS

Whenever a foreign object is introduced into an aqueous system it will tend to adsorb and/or desorb chemical constituents. This will continue until the rates of adsorption and desorption are equal and equilibrium is obtained. The amount of time required to reach equilibrium is a function the capacity of the foreign object to hold specific constituents, the concentrations of the constituents in the aqueous system, the amount of foreign material, and the volume of water which the object is exposed.

In the case of the groundwater monitoring wells constructed at ASARCO, objects such as PVC well screen, gravel pack, and potentially drill cuttings from above the zone of saturation were introduced into the groundwater system. PVC well screen

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and silica gravel pack have limited capacities to adsorb and store chemical constituent and should reach equilibrium with the surrounding water quickly.

Drill cuttings introduced from above the zone of saturation can absorb significant amounts of chemical constituents if they have high Cation Exchange Capacities (CEC) and exist in large quantities. If these conditions are met, drill cuttings will adsorb and desorb metal ions until sufficient aquifer water is flushed past the material for equilibrium to be reached. This may occur through natural groundwater flow, through bailing prior to samplings, and well development.

Due to the high turbidity observed in the ASARCO monitoring well samples, it has been suggested that the colloidal material associated with the turbidity is acting as a sink for metal cations. More specifically, that the cation exchange sites on the colloidal materials is preferentially adsorbing the small, more highly charged ions such as  $\text{Cr}^{+3}$  and  $\text{Pb}^{+2}$  in exchange for larger, less highly charged ions such as  $\text{Na}^{+}$ ,  $\text{Ca}^{+2}$ , and  $\text{Mg}^{+2}$ .

This exchange of cations will only occur if the materials producing the turbidity is introduced from an area outside of the aquifer being monitored. All materials within the aquifer should be in equilibrium with the aquifer due to their long contact time with the aquifer water and its dissolved metals.

The monitoring wells at ASARCO were constructed using hollow stem and air rotary drilling methods. Neither of these drilling methods involved circulation of drill cuttings. Drill cuttings were removed directly from the hole either through the mechanical action of the auger or the air lift of the air rotary rig. This leads to the conclusion that the colloidal material observed in the well came from the saturated zone.

The worst case would be if all turbidity is caused by materials carried down from above the water table and that the material has a high cation exchange capacity. Under these conditions it is likely that this material would come to equilibrium quickly due to water carried through the material during well purging, well development, and by natural flow of groundwater during the one month between well completion and sampling.



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Attempts to estimate the volume of water required to bring a fixed amount of colloidal materials to equilibrium with the water quality were made. These calculations could not be made due to the complex chemical reaction involved. Despite this, it may be stated that adsorption and desorption of metal ions by colloidal material probably had little effect upon the water quality of the samples obtained from the groundwater monitoring wells. This statement can be made since it is likely only small amounts of material was introduced from above the water table and this material in all likelihood reached equilibrium with the formation water prior to sampling.

#### CONCLUSIONS AND RECOMMENDATIONS

The collection of representative samples from groundwater monitoring wells is not a straightforward or easily accomplished task. It requires careful consideration of the hydrologic and chemical conditions existing at each monitoring location. The questions concerning the representativeness of the groundwater samples obtained from ASARCO during the first quarterly sampling is a good case in point.

Due to delays which occurred between sample collection and preservation, the potential for metal ion precipitation and subsequent removal through filtration exists. The degree to which this occurred is difficult to assess due to a lack of data defining the samples' chemical characteristics (pH & Eh) immediately after sampling. At present it can only be stated that the samples have a potentially negative bias for some metal ions (metals concentrations less than actual).

More specific conclusions could be made if additional information is obtained on the amount of time each sample was allowed to stand prior to preservation, and under what conditions each sample was stored during this time.

Due to the high turbidity found in the monitoring wells, the potential for colloidal material to act as a sink for metal ions exists. Based upon the available information concerning the methods of drilling and the time between well completion and sampling, it appears that this is not an important issue. Still it is not possible to totally disregard this issue.

Additional information which would aid in evaluation of this issue includes the volumes of water removed during well

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development at each well and relative degrees of turbidity encountered at each well.

Since the representativeness of the water samples cannot be clearly established at this time, decisions must be made regarding resolution of the issues. Steps taken toward resolution of the issues should include:

- o Obtain the information mentioned in the previous paragraphs and attempt to identify specific wells where the issues discussed are important.
- o Compare the first quarter's analysis with future data to see if the results appear to be representative of the groundwater quality at each site.
- o If the data cannot be validated through these two steps, obtain another quarterly sample from the wells in January of 1986.

An additional option for resolution of the issues has been proposed by Hydrometrics in their letter to Mr. Gene Taylor of the EPA, April 12, 1985 (Attachment C). In this letter they propose to split metal samples. One split will be filtered and acidified, the other acidified and then filtered .5 to 1 hour later. Hydrometrics feels that this will "provide some information on the relationship between metal concentrations and turbidity." If no difference is seen between the samples it may be stated that neither the turbidity or the delays in sample preservation affected metal ion concentrations.

Hydrometrics' proposal has several limitations. First of all it seems unlikely that a significant difference will not exist between the samples. Secondly, the geochemical environment during the next sampling round may be very different from that which existed in January. Despite these limitations the idea does have merit and is worth considering.

In order to remove these issues from future groundwater samplings, the following recommendation is made:

All metals samples should be filtered and preserved immediately after sampling. If turbidity continues to inhibit sample filtration, two options are available. Step filtration system may be used. These systems use

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multiple filters of varying size and work quite effectively on turbid samples. If this is not feasible, a nondisruptive method of borehole evacuation should be used (i.e., bladder pump). Use of a bailer to evacuate a monitoring well will surge the well and disrupt sediments within the formation. Bladder pumps remove water at low rates (1 to 2 gallons per minute) and tend not to disrupt the sediments and, hence, yield samples with low turbidity.

#### REFERENCES

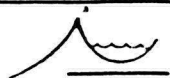
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DE/ASARC5/rg001



ATTACHMENT A





February 19, 1985

Jon Nickel  
Environmental Scientist  
ASARCO, Inc.  
P. O. Box G  
East Helena, Montana 59635

Dear Jon,

Groundwater samples from recently completed monitoring wells DH-1 through DH-11 were collected January 14 through January 21, 1985. Oversight for EPA of field collection of groundwater samples was conducted by personnel from Systems Technology (Systech). Systech collected splits of all groundwater samples obtained by Hydrometrics. I understood the samples were to be sent to the EPA contract laboratory previously used by CH<sub>2</sub>M Hill for analysis of surface and groundwater sample splits obtained from the November 1984 sampling period.

During groundwater sampling of eleven monitoring wells in January, oversight personnel expressed some concerns about sample methods and field parameter measurement. The following summarizes the concerns, describes actions by Hydrometrics to evaluate the concerns and lists conclusions from the information obtained.

1) CONCERN:

The pH measured at Hydrometrics may not be representative of immediate field pH due to CO<sub>2</sub> equilibrium.

If pH changed significantly between the sample filtration and the time of sampling it could influence dissolved metals. Due to turbidity, some samples were allowed to settle for one to three hours before filtration. The concern was that this allowed time for a pH change. This concern was relayed to Hydrometrics by CH<sub>2</sub>M-Hill on January 18, 1985. In the conversation, Hydrometrics stated that they did not expect a significant pH change in the samples during the sample handling time.

#### EVALUATION:

The eleven monitoring wells at ASARCO are completed in the uppermost zone of saturation. Groundwater from shallow aquifers are commonly at or near equilibrium with the atmosphere and rapid loss of CO<sub>2</sub> normally does not occur. The samples were alkaline and well buffered.

Because transportation of water samples from ASARCO's plant site area to Hydrometrics' laboratory takes about eight minutes, a pH reading using Hydrometrics' Orion Model 407A/F specific ion meter (see p. 79 of ASARCO QAAP) is essentially as fast as field measurements but with the advantages of better accuracy under lab conditions. pH readings performed at several intervals after sampling (see Table 1) showed no significant changes in pH up to one day after the water was sampled. Field pH obtained by Systec, using their small Markison field unit, agreed fairly well with measurements in Hydrometrics' laboratory (Table 2).



in constant use during this time. Comparison of the measured SC of exposed standards with measured SC of unexposed standard shows no changes occurred from exposure to ammonia fumes (Table 3).

b) Influences from turbidity

Samples retained from monitoring wells DH-11 (AEH-8501-125) and DH-7 (AEH-8501-122) were used to examine turbidity affects on SC. Measured SC of clear decant from these samples was compared with measured SC of shaken turbid samples. No significant change in SC was observed (see Table 4). Specific conductivity was also measured on turbid shaken samples of DH-11 and the filtrate of DH-11. The water was filtered through a .45 micron filter to remove all suspended material. SC of the filtrate was then measured using Hydrometrics' conductivity bridge. No significant changes in SC was observed (see Table 4).

c) Problems with one of the instruments

Comparison of Systec SC instruments and Hydrometrics' instruments were conducted in Hydrometrics' laboratory January 30, 1985. Samples were measured under both laboratory and outdoor conditions. Samples used for comparison measurement were waters retained by Hydrometrics from well DH-11 (AEH-8501-126-sampled 1-

TABLE 1. PH MEASUREMENTS OVER TIME

<u>Sample No.</u>	<u>Time Coll.</u>	<u>Date</u>	<u>Sample Temp.</u> <u>1st Read.</u> <u>(~10 min.)</u>	<u>pH</u> <u>1st Read.</u> <u>(~10 min.)</u>	<u>Sample Temp.</u> <u>2nd Read.</u> <u>(45 min.)</u>	<u>pH</u> <u>2nd Read.</u> <u>(45 min.)</u>	<u>Sample Temp.</u> <u>3rd Read.</u> <u>(1 day)</u>	<u>pH</u> <u>3rd Read.</u> <u>(1 day)</u>
AEH-8501-119	9:30 A.M.	1/18/85	10°C	7.65	25°C	7.65	25°C	7.90
AEH-8501-124	11:30 A.M.	1/18/85	10.5°C	7.70	25°C	7.71	25°C	7.70
AEH-8501-117	12:30 P.M.	1/18/85	10°C	7.78	25°C	7.79	25°C	7.38
AEH-8501-122	3:00 P.M.	1/18/85	10°C	7.69	25°C	7.65	25°C	7.65
AEH-8501-125	4:30 P.M.	1/18/85	10°C	7.97	25°C	7.71	25°C	7.70
AEH-8501-121	9:30 A.M.	1/19/85	12°C	7.70	25°C	7.69	25°C	7.69
AEH-8501-126	4:20 P.M.	1/21/85	10°C	7.49	25°C	7.52	25°C	7.55

Note: In all cases, sample temperatures and buffer temperatures are the same.

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## CONCLUSION:

Time delays experienced in pH measurement had no significant effect on observed pH. After review of pH measurements over time (Table 1) and comparison with Hydrometrics' measurements with Systec measurements, it is concluded that bringing the sample back to the Hydrometrics' laboratory probably increased the accuracy of the "field" pH measurement. Additionally, the data shows no significant pH change during the time required to filter the sample.

## 2. CONCERN:

There may be changes in measured specific electrical conductance of samples due to ammonia in the laboratory atmosphere and/or turbidity in the samples.

Hydrometrics measures specific conductivity in its laboratory as soon as possible after sample collection. Transportation time from the ASARCO site is about eight minutes. Samples are brought to a 25°C temperature and measured with a Beckman RC-18A conductivity bridge (as described on P. 72 in ASARCO's QAAP). Specific conductivity values collected by Systec were measured at the sampling site using a portable YSI unit. Hydrometrics was notified of the discrepancies of the SC measurements during a conference call that included M. K. Botz and Bob Miller of Hydrometrics, Doug Lovell and John Lucero from CH<sub>2</sub>M-Hill, Rob Green from Water Quality Bureau and Dick Karp from Systec. Dick



TABLE 2. COMPARISON OF TEMPERATURE PH AND SPECIFIC  
CONDUCTIVITY COLLECTED BY SYSTEC AND HYDROMETRICS

<u>Station No.</u>	<u>Sample Date/Time</u>	<u>Field Temp.(°C)</u>		<u>pH</u>		<u>Specific Conductivity</u>	
		<u>Systec/Hydro.</u>		<u>Systec/Hydro*</u>		<u>(umhos/cm)</u>	
AEH-8501-118	1/18/85-0930	7.5	8.0	7.3	7.65	390	458
AEH-8501-124	1/18/85-1130	9.5	9.5	7.25		1870	2006
AEH-8501-117	1/18/85-1245	8.2	9.0	7.5	7.78	490	567
AEH-8501-122	1/18/85-1515	9.0	-	7.6		290	372
AEH-8501-125	1/18/85-1700	3.5	-	7.25	7.97	1180	1197
AEH-8501-126	1/21/85-1630	10.0	10.0	7.4	7.49	310	349

\*Measured in Hydrometrics' laboratory.

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Karp stated he believed his field instrument was functioning correctly and voiced the following theories for the discrepancies:

- a) SC changes in the Hydrometrics' laboratory may result from exposure to ammonia fumes that occasionally emanate from a printing machine in a room adjacent to the Hydrometrics' lab.
- b) SC changes may be related to turbidity of the sample.
- c) There may be a problem with one of the instruments.

During the conference call, Hydrometrics stated that they did not believe that ammonia or suspended solids significantly effected SC measurement and their laboratory instrument was functioning properly.

#### EVALUATION:

Several experiments were performed in Hydrometrics' laboratory to examine the expressed concerns.

- a) Influences from ammonia

Standards used by Hydrometrics for laboratory measurement of SC were exposed in open containers directly on top of the print machine for 3½ hours. The machine was

TABLE 3. COMPARISON OF SPECIFIC CONDUCTIVITY OF STANDARDS  
EXPOSED TO AMMONIA AND UNEXPOSED STANDARDS

The following SC standards were tested after exposure to ammonia with  
print machine running for 3½ hours. Samples were set on top of the  
machine open (1/29/85).

<u>Standard</u>	<u>SC Reading</u>	<u>Time</u>
147	149.8	12:00
717.8	716.1	12:00
1413	1406.2	12:00

SC Standards not exposed to fumes  
(directly from Standard Container):

147	150.0	12:00
717.8	716.0	12:00
1413	1406.3	12:00
717.8	716.0	12:00

TABLE 4. SPECIFIC CONDUCTIVITIES OF DECANTED (CLEAR) SHAKEN  
SAMPLES (HIGH TURBIDITY) AND FILTERED SAMPLE

<u>Sample No.</u>	<u>Date</u>	<u>Cell Factor</u>	<u>Sample Temp.</u>	<u>SC (umhos)</u>
AEH-8501-126 Clear Water decant	1-30-85	.998	25°C	492.2
AEH-8501-126 Sample shaken and turbid	1-30-85	.998	25°C	495.4
AEH-8501-126 Filtered	1-30-85	.998	25°C	490.5
AEH-8501-122 Clear Water decant	1-30-85	.998	25°C	377.0
AEH-8501-122 Sample shaken and turbid	1-30-85	.998	25°C	377.4

15-85) and DH-2 (AEH-8501-117). A comparison of Hydrometrics' lab measured SC and Systec SC measurements is in Table 5. Table 6 contains notes collected by R. Carp at the time of the SC instrument comparisons. Outdoor measurements of SC using Systec's YSI meter were much lower than SC measurements in the laboratory.

Comparison of temperatures measured using the Systec YSI probe and measurements by thermometer indicates some of the indoor-outdoor measurement discrepancies result from inaccurate temperature measurements by the Systec's YSI probe. Systec measures standard temperatures in 100 ml bottles. The amount of water held in these bottles is enough to immerse the SC probe but allows the temperature sensor to be partially exposed to the air. The result is the YSI measured temperatures are between actual standard temperatures and the air temperatures (about -5°F during the test). Table 5 shows that probe-measured temperatures are significantly lower under field conditions than thermometer-measured temperatures. The result is an erroneous temperature correction and consequently an inaccurate SC.



TABLE 5. COMPARISON OF SPECIFIC CONDUCTIVITIES MEASURED BY SYSTEC'S YSI-33 AND BY HYDROMETRICS' LABORATORY

Specific conductivity in umhos of specific samples measured in Hydrometrics' laboratory 1-30-85.

	YSI (Systec)		Beckman SC Meter (Hydrometrics)	
	<u>T°C</u>	<u>SC</u>	<u>T°C</u>	<u>SC</u>
DH-2 (AEH-8501-117)	22.6	552	25	567
DH-11 (AEH-8501-126) (Filtered)	22.0	446	25	491
DH-11 (Unfiltered)	-	-	25	492

Specific conductivity in umhos of samples measured out-of-doors under simulated field conditions using YSI meter.

	<u>T°C</u>		<u>Cell Factor</u>		<u>Corrected SC</u>	
	<u>YSI Inst.</u>	<u>Therm.</u>	<u>Using YSI Measured Temp.</u>	<u>Using Therm. Temp.</u>	<u>Using YSI Measured Temp.</u>	<u>Using Therm. Temp.</u>
147 St.	1.5	(8.0)	.705	(.863)		
718 St	3.5	(9.0)	.829	(.977)		
DH-2	<0	(5.0)	-	-	409	(487)
DH-11	<0	(5.5)	-	-	371	(443)

- NOTES:
1. Table is a composite of notes collected by R. Karp in Hydrometrics' Lab and Hydro-Lab Book Records.
  2. Temperatures and SC recorded by YSI in lab are averages of several measurements.
  3. YSI measured temperature incorrectly. Corrected temperatures using thermometer and subsequent calculation are in parenthesis.
  4. Outside temperature approximately -5°F.
  5. YSI Probe unable to measure Sample Temperature - Calculated SC used temperatures measured by thermometer.

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TABLE 6  
DATA RECEIVED FROM R. KARP  
FROM SPECIFIC CONDUCTIVITY TESTS

② HADRC @ 1045

① J.H. YSI 33 (54575) w/ 147 & 717.8 } run at 25°C  
 DH-2 (117)  
 Run DH-2 (122)

② Filter DH-H '125'

Run w/ B.C. YSI 33 & Beckman

@ 1205 Rain standards 147 & 717.8

Machine 3215

Red line OK

147 std	Temp °C	Machine	13"	Temp °C	153.4	.959
	20.5		140		153.2	.965
	21.4		142		152.5	.964
	21.8		148		157.6	.933
	22.0		149		158.1	.930
					160	.949

717.8	22.0	720		163.8	.940
	22.0	710		153.7	.953
	22.5	700		135.1	.976
	22.9	700		125.3	.984
				110	.963

DH-2 (117)	22.1	540		595.8	
	22.6	550		570.4	
	23.0	535		550.7	
		540		570.1	(552)
	22.3	550			

DE-11

Temp  
20°  
21°  
Reading  
Temp Cor.

21.9	434	461.3
22.0	540*	530.4*
22.0	400	466.7
22.0	520*	530.4*
22.0	446	473.1

Ave 467.0 (.957) 446.8

Noted that if wire is not submerged temp is off by several degrees ~ 2-3°C

B30455 - HYDRO DE-11 F - 487.5 490.5

Temp	Reading	TCF	Temp (at SC)	cell	2-2
1.5 (80.8)	115	1.814 (1.491)	208.7 (170.3)	0.705 (1.863)	

717.8	3.5 (90.2)	510	1.697 (1.44)	865.4 (734.4)	829 (1.977)
-------	------------	-----	--------------	---------------	-------------

DE-11 F (126)	5.0	215	1.618	477.3 (1.77 (1.92))	371 (443)
---------------	-----	-----	-------	---------------------	-----------

DE-2 (117)	5.5	326	1.593	519.5	786 (1.937)	409 (487)
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Temps in ( ) are therm. readings

$$TCF = 51 + (T_w - 25)^{1.7}$$



Table 5 also suggests that even with corrected temperature measurements, the YSI field instrument is influenced by extreme temperatures.

CONCLUSION:

Tests showed no measurable influence on SC from turbidity or ammonia fumes. Specific conductivity measurement discrepancies by Hydrometrics and Systec are the result of inaccurate measurement temperatures using the Systec field instrument.

3) CONCERN:

Specific conductivity measurement of water collected at monitoring well DH-11 (AEH-8501-126) are different before and after pumping of this well.

Similar to the rest of the monitoring wells, DH-11 was originally developed by bailing. Bailing was used because it was required to handle the water as a hazardous waste and below freezing (commonly below 0°F) conditions made pumping difficult. Bailing also is quite successful to clean-up a well. Water samples were obtained after bailing more than six times the bore volume of the well. Because samples collected on 1-15-85 were too turbid to filter, DH-11 was redeveloped by pumping and resampled on 1-21-85. Measured specific conductivity of samples collected 1-15-85 and 1-21-85 were 492 and 349 umhos, respectively as measured by

Hydrometrics. Samples collected 1-21-85 were less turbid than those collected 1-15-85.

#### EVALUATION:

Samples retained from both dates were remeasured for SC and the relative differences confirmed. As previously described, SC experiments run on turbid, clear decant and filtered samples indicate there is no relationship between turbidity and specific conductivity of samples collected at ASARCO.

#### CONCLUSION:

No definite conclusions about the observed SC differences can be drawn at this time. Well DH-11 is shallow and is located about 20 to 30 feet away from Prickly Pear Creek. During pumping of the estimated 400 gallons to develop the well, groundwater at DH-11 may have received some recharge from the creek. January measurement of Prickly Pear Creek show specific conductivity ranged 305 to 313 umhos. Conductivity changes due to pumping wells adjacent to a stream are not unusual and this may be the cause of the SC difference.

#### 4) CONCERN:

The temperature correction factor shown for the field SC survey on P. 43 of the ASARCO QAPP is not the same as described in Standard Methods for Examination of Water and Wastewater, 15th Edition, 1980.

## EVALUATION:

SC measurement of sampled waters is performed in Hydrometric's laboratory at 25°C as described on pp. 72-78 ASARCO QAPP. Temperature correction factors are not needed or used in final SC calculations. The form shown in the QAPP is not the form used for the laboratory. All temperature and cell correction factors are corrected using a computerized program which is consistent with standard methods and with USDA Agricultural Handbook 60.

## CONCLUSION:

If SC measurements are taken using field instruments, published temperatures correction factor formula from Standard Methods or other equivalent methods will be used.

If you have any questions, please call me.

Sincerely,



Robert J. Miller  
Hydrogeologist

RJM:jy

cc: Doug Lovell, CH<sub>2</sub>M-Hill



ATTACHMENT B





# Systems Technology, Inc.

Environmental Systems Engineering

## TECHNICAL MEMORANDUM

Steamboat Block  
616 Helena Ave.  
Helena, MT 59601  
(406) 443-5277

Date: April 30, 1985

Subject: ASARCO RI; Groundwater Turbidity

To: John Lucero, CH2M HILL

FROM: Dick Karp, SYSTEC *Dick Karp*

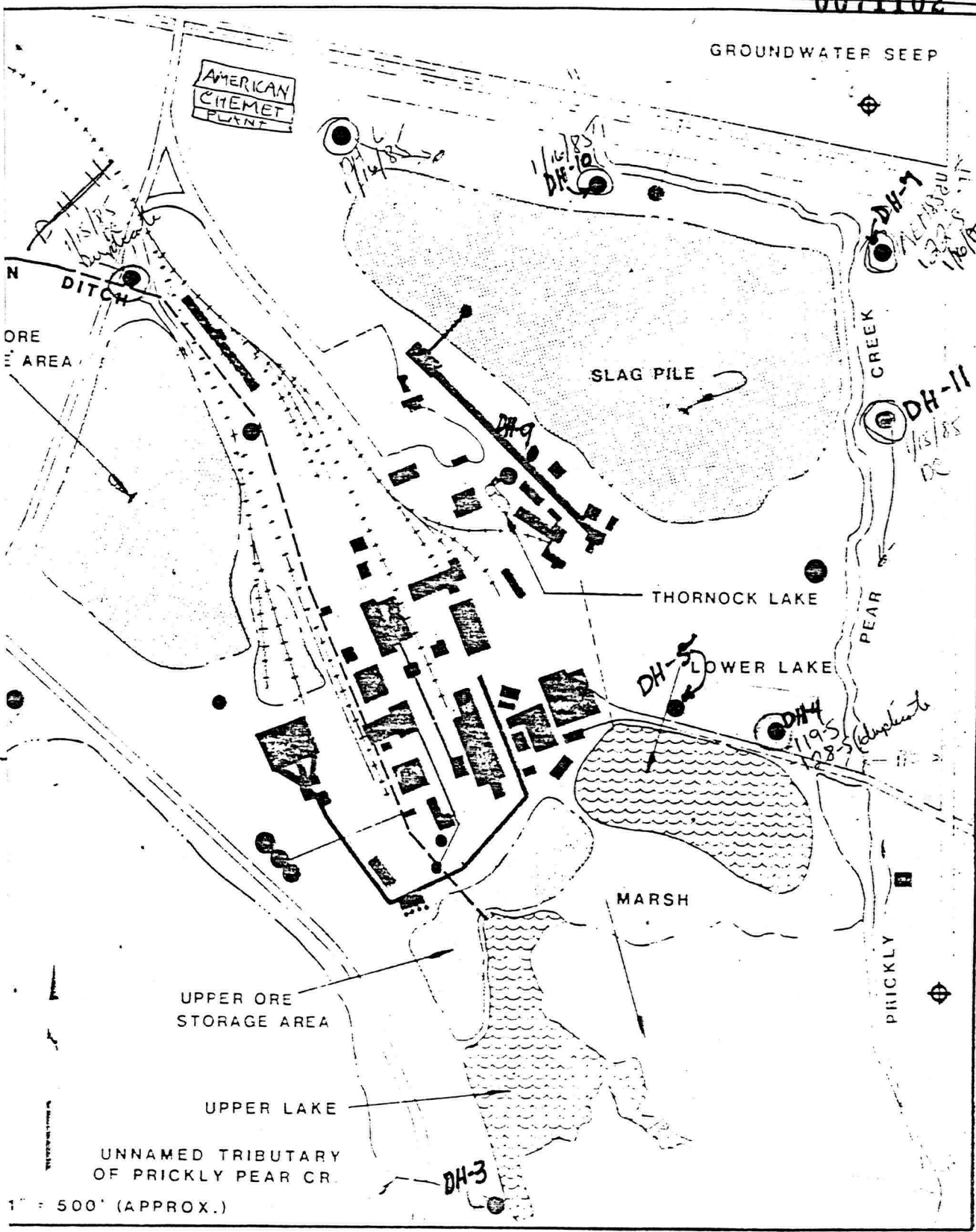
During the first groundwater sampling episode (January 15th thru 21st, 1985), concern was raised about the turbidity of the samples. This concern focused on the issue of whether the turbidity was indicative of inadequately developed wells, and further, whether this implied non representativeness of the samples.

It seems unlikely to me that the turbidity observed actually exists in the aquifer. It seems more likely that the turbidity is a result of entraining the mud-cake material on the wall of the well hole which was generated during well installation (see enclosure). The problems encountered with filtering of samples due to this turbidity also suggested the presences of colloidal clays. Even though there maybe a significant amount of colloidal clay in the aquifer, the turbidity of the samples seems to indicate that the groundwater maybe introduced to more clay during bailing. Thus the sample may have a larger clay content than the actual water in the aquifer. This increased clay content may provide more adsorption sites for metals. Thus metals that are dissolved in the aquifer became adsorbed when introduced to the increased clay content at the well and are then subsequently filtered out when the water drawn for a sample is filtered. The sample analyzed for dissolved metals would then yield results less than what actually exists in the aquifer.

In response to this concern the EPA oversight personnel (i.e. Dick Karp) collected samples for total metals (i.e. unfiltered acidified) from a number of wells sampled during this first episode. The following tabulation lists the information which specifies the total metals samples.

<u>Well No.</u>	<u>Station Location</u>	<u>ITR Code</u>	<u>Tag No</u>	<u>Sample Date/time</u>
DH-2	AEH8501-117-S	MHA-528	8-12938	1/18/85-1245
DH-3	AEH8501-118-S	MHA-525	8-12941	1/18/85-0930
DH-3R	AEH8501-130-S	MHA-526	8-12940	1/18/85-0930
DH-7	AEH8501-122-S	MHA-529	8-12952	1/18/85-1515
DH-9	AEH8501-124-S	MHA-527	8-12946	1/18/85-1130
DH-10	AEH8501-125-S	MHA-530	8-12953	1/18/85-1700

sure 1



NT SITE MONITORING WELLS

● SHALLOW WELL

FIGURE 1  
PLAN MAP OF ASARCO  
EAST HELENA PLANT FACILITIES

PREPARED BY:  
HYDROMETRICS

17-5. Bibliography  
[1] "Well Drilling, Operations, Department of the Army Technical Manual 5-297, Washington, D.C., September 1965.  
[2] "Ground Water and Wells," UOP Johnson Division, St. Paul, Minn., 1966.

The location of these wells are as shown on the accompanying figure (i.e. Figure 1., Plan Map of ASARCO as prepared by HYDROMETRICS). The following table compares the dissolved metals (i.e. As, Cd, Cu, Fe, Pb, Mn & Zn) concentrations (i.e. in ug/l, ppb) reported by ASARCO with the totals reported by EPA for the same well sample.

Comparison of USEPA &amp; ASARCO Metals Data

Well No.	As		Cd		Cu		Fe		Pb		Mn		Zn	
	EPA	ASR	EPA	ASR	EPA	ASR	EPA	ASR	EPA	ASR	EPA	ASR	EPA	ASR
DH-2	26	8.	4.	<1.	61	28.	18,300	25.	45	45.	247	19.	349	110
DH-3	7.8	7.	4.	<1.	6.4	48.	111	63.	4.6	45.	101	120	156	180
DH-3R	5.4	1.	4.	3.	18.	48.	5780	25.	11	45.	196	100	155	170
DH-7	99	5.	4.	<1.	343	48.	62500	25.	51	45.	4390	41	341	11
DH-9	22,000	6.	500	5.	5500	13.	219,000	130	26000	45.	12400	2800	48100	580
DH-10	5800	5100	4.	3.	156	9.	16,600	63	170	45.	4310	4800	551	71

For some of these well samples (e.g. DH-9, DH-7) the difference between the EPA total metals and ASARCO dissolved metals is very significant. The analytical procedure for metals apparently involves a digestion step (i.e. CLP SOW No. 784). This means that the results for the EPA total metals represent the dissolved fraction, the adsorbed fraction plus any metals associated with the suspended material matrix. These large differences suggest that there is more than just dissolved and matrix fractions of metal, but rather, that there maybe a sizeable quantity of the adsorbed fraction. For the sample from DH-9, the CLP reported a high aluminum content (i.e. Al = 167,000 ppb) which would further support the clay type of suspended material.

Another incident that occurred during the first sampling episode which may cast some doubt on the representativeness of the samples was the change observed in well number DH-11 after pumping to clarity. DH-11 was sampled on January 15, 1985, however, this sample was so turbid, presumably with colloidal clays, it would not filter. Another sample was collected on January 21, 1985 after the well had been sufficiently pumped to produce clear water. This sample filtered readily. DH-11 is sample location AEH8501-126. HYDROMETRICS reported an electrical conductivity of 492 umhos/cm @ 25 C for the sample collected on 1/15/85, and 349 umhos/cm @ 25 C for the sample collected on 1/21/85. This difference may indicate that the well was insufficiently pumped on the 15th. (see enclosure 2) HYDRO personnel suggested that the lower conductivity observed on the 21st may be due to the influence of Prickley Pear Creek. Some rough calculations made by SYSTEC's staff hydrogeologist (Kevin Jones) do not support HYDRO's conjecture. (see enclosure 3)

For all the wells sampled, the smallest TSS value was reported for DH-11 (1/21/85); 3.3 mg/l. With the exception of DH-5 (AEH8501-120)

## 2.G.2.a. SPECIFIC CONDUCTANCE

Enclosure 2  
0071104

The specific conductance of a water sample is a measure of its ability to carry an electrical current under specific conditions. Specific conductance, which is a measure of the ionized salts, gives an indication of the concentration of dissolved solids in the water.

There are several reasons for determining the specific conductance of a sample in the field at the time of collection rather than waiting for a laboratory measurement. The field determination can be used as an aid in evaluating whether a sample is representative of water in the aquifer. For example, in new or little used wells, or in wells that have been recently drilled, grouted, or cemented, chemical changes in the pumped water may be rather large, and the well may require prolonged pumping to insure that the sample is representative of water in the aquifer. Specific-conductance determinations can be used to indicate that sufficient water has been pumped and that the quality of the water is stabilized.

A specific-conductance value that is markedly different from values obtained in nearby wells may indicate a different source of water, such as induced recharge, contamination from the surface, or leakage from a formation that contains water of different quality. Detection of an anomaly may indicate that more detailed sampling or reevaluation of the well is required. If so, the work can usually be done more economically at the time the original sample is collected rather than several weeks or months later.

Once the sample is in the container, its specific conductance may change with time as a result of precipitation of minerals from the water. A sample that has been acidified or otherwise treated will not yield an accurate representation of the specific conductance of the water in the aquifer; therefore, it is essential to obtain an accurate field determination.

## 2.G.2.a.1. METHOD SUMMARY

The ability of a solution to conduct an electrical current is a function of the concentration and charge of the ions in solution and of the rate at which the ions can move under the influence of an electrical potential. As the number of ions per unit volume of solution increases, the rate at which individual ions can move decreases because of interionic attraction and other effects. A graph of total ion concentration versus specific conductance, even for solutions of a single salt, is a straight line only for values below 1,000 micromhos/cm. As specific conductance increases to above 5,000 micromhos/cm, the regression line curves significantly; beyond 50,000 micromhos/cm, the specific conductance may be an unsatisfactory index of ion concentration.

The temperature of the electrolyte affects the ionic velocities, and consequently, the specific conductance. For example, the specific conductance of potassium chloride (KCl) solutions changes about 2 percent per degree Celsius near 25°C.

Specific-conductance meters used in the field should be battery operated, equipped with temperature compensator, and read directly in micromhos/cm at 25°C. The direct reading meter is recommended to save time in converting resistance values to specific conductance and to insure that the value is read in the field.

The cell should be checked before initial use and should be checked daily during regular use. A 0.00702 N potassium chloride (KCl) solution (dissolve 0.5234 g KCl dried at 180°C for 1 hour in distilled water and dilute to exactly 1 litre) has a specific conductance of 1,000 micromhos/cm at 25°C. Routine checks are made by using the 0.00702 N standard solution at the ambient temperature. The temperature control on the instrument is set at 25°C, and the ambient temperature of the standard KCl solution is recorded. A value of specific conductance is obtained and compared with the values given in figure 2-32 for the ambient temperature. The value obtained should be within 5 percent of that in figure 2-32.

Next, the temperature-adjustment knob is moved to the ambient temperature, and the meter is read. The value obtained should be 1,000 micromhos/cm, regardless of the ambient temperature.



4/2/85

0071105

In order to calculate the break through time for a pumping well ~~is~~ next to a river the following equation can be used

$$t_0 = \frac{7.48 p a^2}{3 K s} \ln \left( \frac{2a}{r_w} \right)$$

Solute travel times  
(Kirkham & Alley 1975)

where

$t_0$  = breakthrough time in days

$p$  = effective porosity

$a$  = distance from stream to pumped well

$K$  = Hydraulic Conductivity of aquifer  $gpd/ft^2$

$s$  = drawdown

note: 1) assumes a sharp front  
2) steady state drawdown  
3) provides a conservative approach (ie sooner breakthrough than actual)

Some typical evaluations for clean gravel  
(basically an ideal high yield aquifer)

10 = $s$	2 hrs of pumping	10 ft
150 = $a$		150
.5 = $r_w$		.5
100,000 = $K$ = clean gravel		1,000
.5 = $p$		.25
.25 = $s$		

8.9 days

10 = $s$	4 hrs	10
150 = $a$		150
.5 = $r_w$		.5
100,000 = $K$		1,000
.5 = $p$		.5

17.94 days

## Silty aquifer

a	10		10	
S	150		150	
R <sub>0</sub>	.5	179 days	.5	1794 days
K	100		10	
P	.5		.5	
	10		10	
	150		150	
	.5	89	.5	897
	100		10	
	.25		.25	

These number compare well with published studies. I am making "textbook" assumptions for the K & P values however it does give an idea on the length of time necessary for breakthrough. If the aquifer is full of clay & low yield as Hydro claims the idea a breakthrough ~~is~~ occurring is extremely far fetched. My own feeling is that it would occur in the 8-10 day range.

Some ref. that discuss sampling & turbid wells problem. (indicates completion)

Guidelines for sampling GW Journal WPCF Vol 55 #1  
1/83

USGS Techniques for Water Resource Inves.

Book 1 Chapt D2 and Book 5 Chapt A1

National Handbook of Methods for H<sub>2</sub>O data acquisition

These are basic, I have a detailed listing if your interested

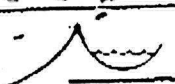
which reportedly had a TSS of 36 mg/l, all the other wells had TSS values greater than 295 mg/l, the highest being 5540 mg/l for DH-8 (AEH8501-123). These TSS values are indicative of highly turbid samples.

In response to these concerns over turbidity HYDRO and ASARCO proposed to acidify a sample before filtering, allow the sample to set and then filter. This sample would then be analyzed for metals and compared with a sample filtered and then acidified, the thought being that acidifying first would strip any metals adhering to clay. HYDRO reportedly collected three such samples during the second sampling episode (4/8-11/85). Of interest is the selection of DH-5 for one of these samples. As was mentioned, DH-5 displayed the least amount of suspended solid of any of the bailed wells during the first sampling episode. Thus this well would not appear to be a good selection for demonstrating to what extent the excessive turbidity may affect metal concentrations.



ATTACHMENT C





## HYDROMETRICS

April 12, 1985

ENVIRONMENTAL PROTECTION  
AGENCY

APR 12 1985

Mr. Gene Taylor  
Environmental Protection Agency  
Federal Building  
Helena, Montana 59626

MONTANA OFFICE

RE: ASARCO East Helena Smelter  
Water Resources Investigation

Dear Mr. Taylor:

As discussed in phone conversations with you, Doug Lovell, Bob Miller and myself on March 22, 1985, it is Hydrometrics' recommendation that future monitoring well sampling procedures remain similar to previous procedures.

Sampling procedures will include removal of at least three well bore volumes by bailing. We feel that extended pumping of wells located near Prickly Pear Creek may induce stream water into the wells. Samples from these wells would, therefore, be more representative of stream water quality than natural groundwater quality. Approximately five of the recently drilled monitoring wells have several feet of water in the well bore and development of these wells by pumping probably is not possible.

Turbidity observed in samples collected in January 1985 should decline in future sampling. As these wells are repeatedly sampled, turbidity should be less of a problem.

Based on groundwater analytical data from the first well sampling, we will handle water from only wells DH-4, DH-6 and DH-10 as hazardous wastes in future sampling.

Based on our conversation, we are developing a schedule of tentative dates for the remainder of the sampling program. It is our understanding that you, in coordination with Jon Nickel of ASARCO, are reviewing the proposed program schedule.

As we discussed in our conversation, we will add nitric acid to three groundwater samples prior to filtration through the 0.45  $\mu$  filter during our next well sampling period. This will provide some information on the relationship between metal concentrations and turbidity. We recommend wells DH-3, DH-5 and DH-6 for this test. The samples will set for .5 to one hour then will be filtered. As requested by Doug Lovell of CH2M-Hill, we have estimated potential changes in the samples due to acidification of suspended solids in the sample. Obviously acidification with nitric acid to pH of less than 2 for one hour should cause dissolution of some metals that, under normal conditions, would not be soluble. Due to their geochemistry and mobility in the system, we expect small increases in zinc and copper (0.01

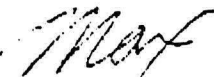


Gene Taylor  
Environmental Protection Agency  
April 12, 1985  
Page Two

to 0.04 mg/l) in the acidified samples. Cadmium should be associated with zinc and small increases in its concentration (0.005 to 0.01 mg/l) may occur. Due to their presence in the drainage system in mines along Prickly Pear Creek and because of their acid solubility, we expect moderate increases in iron concentrations (0.2 to 0.7 mg/l) and lead (0.005 to 0.02 mg/l). Arsenic is not expected to change more than 10 percent from the value reported in the normal samples.

Please call me if you have any questions or need any further information on the sampling program.

Sincerely,



M. K. Botz, P. E.  
Hydrologist/Engineer

MKB:jy

cc: Jon Nickel - ASARCO, East Helena